JOURNAL OF CATALYSIS 71, 434–438 (1981)

Surface-Catalyzed Production of Nitrous Oxide from the Reaction of N Atoms and O_2 on Platinum

The surface-catalyzed reaction of gas-phase N atoms with chemisorbed oxygen on Pt gives N_2O in high yield. N_2O is an uncommon product of surface reactions. The results suggest that it is produced via an adsorbed NO intermediate.

The reaction of a gas-phase atom with an adsorbed species represents the simplest kind of heterogeneous catalysis. Although surface recombination of like atoms has been frequently studied, reactions involving unlike atoms have not (*1–3*). Nevertheless, such systems are of particular interest from the standpoint of reaction energy partitioning. It is predicted, for example, that a Rideal process, involving attack by O on C atoms adsorbed on Pt will yield highly vibrationally excited CO (*4*). This product molecule should be detectable by infrared chemiluminescence. Such a technique would be the surface analog of the gas-phase experiment originated by Cashion and Polanyi (*5*). With this in mind, we investigated a similar, but experimentally simpler, system: the reaction of N atoms with O atom targets chemisorbed on Pt.

We hoped that Pt would catalyze the formation of NO, the simplest molecule that might desorb in an excited state, and emit infrared radiation. In fact it was emission from N_2O that was observed. The excitation was not due to the reaction step and therefore gave no insight on energy partition. However, the process of N_2O formation was so efficient that it merits attention.

I. APPARATUS

The apparatus, shown in Fig. 1, is a fast-flow, low-pressure system comprising a reactor and three reactant inlet lines. The reactor holds a Pt foil assembly and is equipped with a NaCl window positioned in front of an FTIS (Fourier transform infrared spectrometer, Nicolet 7199) inlet aperture. The foil can be electrically heated to a desired temperature as monitored by a thermocouple spot-welded to its center. Nitrogen containing 1 or 2% of atoms generated by a microwave discharge can be admitted to the reactor via several paths. Path A proceeds directly from the discharge to the reactor. Path B is furnished with a water vapor inlet and a dry ice–acetone cold trap which serves to remove vibrationally excited molecules $N_2^\dagger$ also emerging from the discharge. Path C, a bypass, leads from the discharge section to the region downstream from the Pt foil. All of these paths are equipped with glass-encased magnetic slugs attached to small coils of Cu wire. These assemblies serve two purposes. Because their outer diameter is only slightly less than the flow tube inner diameter, the slugs can block the gas flow from a given path when moved into appropriate position by means of an external field. Alternatively, one can position only the Cu coil in the given path. The flow is then not blocked but heterogeneous recombination of N atoms on the coil effectively removes them from the stream. The net result is that reactants can be admitted upstream or downstream of the Pt catalyst foil with either atoms or vibrationally excited molecules selectively removed.

Molecular oxygen is admitted through a separate inlet at about the same rate as N_2.

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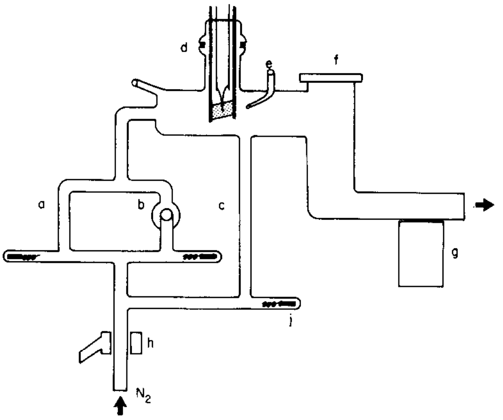

FIG. 1. Fast-flow system for reaction of N and O_2 on Pt. (a), (b), (c) N atom inlets; path B with cold trap; (d) Pt foil assembly; (e) N_2O inlet; (f) NaCl window; (g) photomultiplier; (h) microwave discharge; (i) oxygen inlet.

It is useful to be able to admit controlled flows of N_2O to the system; one N_2O inlet is shown in Fig. 1 emerging immediately downstream of the Pt foil. Typical total gas flow rates are between 500 and 1000 cm^3/min at pressures between 1 and 2 Torr. (1 Torr = 133.3 Nm^{-2}.) Sufficient degassing of the foil is achieved by heating briefly at red heat in the reactive atmosphere and then holding it at operating temperatures of 150–300°C.

The emission observation region is located about 10 cm downstream of the foil. The spectrometer thus surveys through a NaCl window, a cylindrical section of uncollimated radiation (40 mm i.d., ~15 cm length).

II. OBSERVATIONS

A typical emission spectrum is shown in Fig. 2. The sharp peaks at 2220 cm^{-1}, superimposed on the blackbody background radiation, are due to N_2O. We summarize briefly several experiments and observations we made.

1. When the Pt foil is either removed or replaced by Cu, the N_2O spectrum disappears. The emission intensity reaches a maximum at a surface temperature of about 200°C and decreases rapidly at higher temperatures. Thus, N_2O formation is due to catalysis by the Pt surface.

2. With the Pt foil removed and all flow and discharge conditions remaining the same, a small flow of N_2O introduced at the original location of the Pt results in the same spectrum. This spectrum confirms the identity of the emitting species, and also indicates that vibrationally hot $N_2\dagger$ from the discharge is largely responsible for exciting product N_2O to an emitting state. About 10% of all N_2 molecules passing through the discharge are excited to at least the first vibrational level (*6*). Since energy transfer between $N_2\dagger$ and N_2O is nearly resonant, infrared radiation results, just as in the case of $N_2\dagger$–CO mixtures (*7*). Nor is vibrationally hot $N_2\dagger$ effectively deactivated by wall interactions. Quenching requires about 10^4 collisions, so $N_2\dagger$ is present and can excite N_2O throughout the flow path.

3. When paths C and B are closed with two of the glass slugs and the Cu coil on the other slug is placed in path A, the spectrum disappears. Because vibrationally excited $N_2\dagger$ is not quenched on the Cu surface, we conclude that N atoms, which recombine on the Cu surface, are the key reactants rather than $N_2\dagger$.

4. Paths A and C are closed with glass slugs. This procedure directs the flow from the discharge through the dry ice–acetone

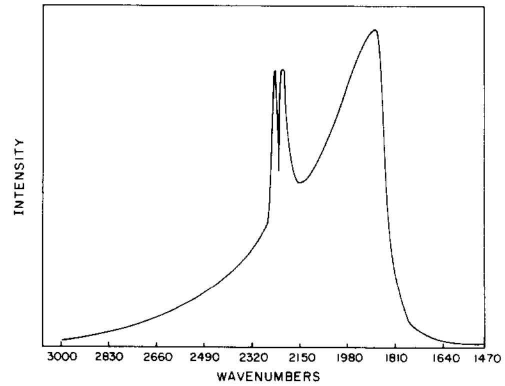

FIG. 2. Infrared emission spectrum: $N + O_2 \xrightarrow[Pt]{} N_2O$. The N_2O peaks appear on a blackbody background emission spectrum.

trap in which water vapor has been previously condensed. The trap quenches the vibrationally excited N_2 but does not appreciably affect the N atom concentration. However, the N_2O emission vanishes, indicating that both N atoms and vibrationally excited N_2 molecules must be present in order to obtain a spectrum. We confirm the presence of N atoms after the trap by monitoring the Lewis–Rayleigh afterglow due to homogeneous N atom recombination. These observations strongly suggest that N atoms are the key reactant in N_2O formation and that $N_2\dagger$ excites the N_2O after it is formed.

5. With paths B and C blocked a stream of N, N_2, and O_2 is passed through path A over the Pt foil. An emission spectrum is obtained. By shifting the slugs we switch the flow to path B which removes $N_2\dagger$ but not N or O_2. The spectrum disappears. We then open path C to allow some of the discharge flow to join the flow from the Pt foil. The spectrum reappears. We conclude that N_2O could be formed on the Pt surface by N atoms and O_2 in the absence of $N_2\dagger$.

6. We estimate the yield of N_2O by removing the Pt foil and introducing N_2O until the radiation intensity matches that observed when the foil was present and N_2O was being produced. The pressure due to injected N_2O is between 4 and 8 μm, about 10 to 20% of the N atom pressure. Clearly, a large fraction of N atoms incident on the Pt foil in the presence of O_2 must be converted to N_2O.

III. DISCUSSION

Because the production rates of N_2O are so high only N and $N_2\dagger$ would seem to qualify as N-containing reactants. The experimental observations strongly suggest that N atoms and chemisorbed oxygen atoms are the key reactant in this efficient production of N_2O at a Pt surface. The role of $N_2\dagger$ is to excite the N_2O in the gas phase after it is formed. Other excited species such as $N_2A^3\Sigma_u^+$ present in *active* nitrogen do not generate N_2O in gas-phase reactions with O_2, and do not occur in sufficient concentrations to explain the levels of N_2O encountered in these experiments (*8*). We neither claim nor deny that the nascent N_2O leaves the surface in a vibrationally excited state. The gas densities in our experiment were high enough that a newly formed N_2O would most likely be quenched by resonant exchange with a ground-state N_2 before being subsequently excited to radiation by collision with a $N_2\dagger$. Nor does the absence of a NO emission spectrum constitute very strong evidence that it is not formed as we had originally hoped it would be. It is unlikely that we would have observed emission from NO if it were present first, because it is rapidly consumed by gas-phase reaction with N atoms to yield N_2 and O, and second, because it cannot be excited by resonant exchange with $N_2\dagger$. Note that every product N_2O makes many collisions with both N_2 and $N_2\dagger$ before reaching the field of view of the FTIS.

Although the surface decomposition of N_2O has been investigated often there are few examples of its heterogeneous production. It appears in ammonia oxidation under restricted conditions and in the reduction of nitrogen oxides by CO (*9*, *10*). It can also arise as a minor product from dissociation of NO on some metals; for example, Ag with coadsorbed Na (*11*). Because the density, flow velocity, and catalyst geometry do not completely free our experiment from diffusion effects, we have not quantitatively investigated the dependence of H_2O production rate on N and O_2 pressures. Nevertheless, from known behavior of N atoms and O_2 on Pt, we can propose a plausible series of reaction steps which should lead to high rates of N_2O formation.

First we note that the decrease in N_2O production as surface temperature increases from 200 to 300°C very much parallels the desorption behavior of NO on Pt (*12*). This similarity suggests that adsorbed NO is an intermediate species. In the second place, because O_2 is in high excess relative to N, and also has a high sticking probability for dissociative adsorption on Pt, the surface is likely to have a high coverage of O atoms. Moreover, O_2 does not desorb from platinum below temperatures of ~500°C. Therefore, a N atom from the gas phase is more likely to encounter an adsorbed O atom and form NO than to find an adsorbed N atom and recombine to form N_2.

The following steps include those most likely to play a significant role in the reaction we have observed:

$$O_2 \rightarrow 2\ O_{ads}, \quad (1)$$

$$N \rightarrow N_{ads}, \quad (2)$$

$$N + O_{ads} \rightarrow NO_{ads}, \quad (3)$$

$$N_{ads} + O_{ads} \rightarrow NO_{ads}, \quad (4)$$

$$NO_{ads} \rightarrow NO\uparrow, \quad (5)$$

$$N + NO_{ads} \rightarrow N_2O \text{ or } N_2O^{\dagger}, \quad (6)$$

$$N_{ads} + NO_{ads} \rightarrow N_2O \text{ or } N_2O^{\dagger}. \quad (7)$$

The formation of adsorbed NO can proceed by a Rideal step (3) or in a Langmuir–Hinshelwood (LH) mode (4). We favor the former somewhat because of the high coverage of O which is likely to be obtained. In principle, the final step which forms N_2O can also be a Rideal mechanism (6) or a Langmuir–Hinshelwood mechanism (7). Again we favor the Rideal step because the N atom coverage is likely to be low since the O atom coverage is high. In addition, since the N surface bond is strong, the LH mechanism must be activated and therefore is energetically less favorable. Finally we note that in the flash desorption of NO from Pt, the only products reported are NO, N_2, and O_2 (*12*). There is no N_2O formed. Evidently the presence of N atoms and NO on a Pt surface does not lead, in the temperature range of interest, to N_2O formation. Consequently, although we do not rule out the possibility of reactions such as (4) and (7), we believe that N_2O is most likely to be formed by a sequence of two Rideal steps such as (3) and (6).

We must also recognize the possibility that NO formed on the surface and desorbed as in step (5) might conceivably react with N or $N_2^{\dagger}$ in the gas phase to form N_2O by

$$N + NO \rightarrow N_2O \quad (8)$$

or

$$N_2^{\dagger} + NO \rightarrow N_2O + N. \quad (9)$$

It is sufficient to note that when we introduced NO into our reactor downstream of a nitrogen discharge we obtained no N_2O spectrum. Moreover, reaction (8) which actually yields (N_2 + O) is so exothermic that the presence of a third body would be required to stabilize any N_2O product, an unlikely possibility at the gas density in our reactor. It is also known that reaction (8) is spin forbidden in the gas phase although on the surface the participation of electrons from the metal substrate in the bonding removes this spin constraint (*13*).

Of the many investigators who have studied the gas-phase reaction of N with O_2 only two have reported the presence of N_2O in the products. Varney (*14*), wishing to determine the role of N^+ ions in the reaction of O_2 with active nitrogen from a discharge, passed both reactants through a series of perforated electrodes. He was able to condense N_2O in a cold trap downstream of the electrode assembly. Neither the materials nor the temperature of the electrodes were specified, but from the diagram of the apparatus it appears that they were close to the discharge and therefore could have been hot. We suggest that the N_2O which he found could have resulted from a surface-catalyzed reaction on the electrodes rather than from a homogeneous gas-phase reaction. In their study of reaction (8) Mavroyannis and Winkler (*15*) reported small amounts of N_2O in a reactor whose surfaces were poisoned with Na_2NPO_4 but not in an unpoisoned reactor. Clearly, surface effects were important.

One final possibility should be noted. The reaction of N atoms with NO_2 is known to yield N_2O as in

$$N + NO_2 \rightarrow N_2O + O. \qquad (10)$$

If NO is produced on the Pt surface in our system it might conceivably desorb and react with O_2 to form NO_2. However, this reaction is a slow termolecular process which should take place to an insignificant extent at the gas densities in our reactor. Consequently, it seems highly unlikely that reaction (10) could contribute to the N_2O formation which we observed.

ACKNOWLEDGMENTS

We gratefully acknowledge support for this work from the National Science Foundation under Grant ENG 7808620 and from the Air Force Office of Scientific Research under Grant F49620-80-C-0026. We also thank Professor Robert Gasser for his helpful comments.

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Received February 25, 1981; revised May 25, 1981